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MECHANISMS OF REACTIONS OF OXIDIZERS

by
A. G. Keenan

Department of Chemistry
University of Miami
Coral Gables, Florida
33124

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A. G. Keenan

Chemistry Department, University of Miami
Coral Gables, Florida 33124

A "Notice of Allowance" has been issued by the Patent Office on the patent "Ammonium Nitrate Explosive Compositions" and it is expected that the patent will be issued in June 1967. The basis of the patent is the synergistic catalysis of ammonium nitrate decomposition by transition metals and a stoichiometric excess of chloride ion. This was described in some detail in Annual Report No. 5, dated 31 May 1966. Patent applications have also been filed in twelve foreign countries.

A problem which now requires concerted effort is to discover a way of translating the laboratory results on synergistic catalysis, which look quite significant, into test results which can be meaningfully evaluated in terms of practical propellant technology. The laboratory results have been obtained by a thermal analysis method in which the sizes of the temperature peaks obtained are a direct function of the particular apparatus and procedures used. However, there can be no doubt that the large catalytic effects observed would be reflected in significant variations in performance under propellant conditions. Technologically significant parameters such as burning rate and specific impulse need to be measured for compositions containing both fuel and synergistically catalyzed oxidizer.

The thermal analysis studies are continuing with attention now being focussed on ammonium perchlorate and composite ammonium nitrate-perchlorate oxidizers. The purpose is to discover whether the principles of synergistic catalysis found for ammonium nitrate decomposition can be applied to these other oxidizer systems. It has been found possible so far to obtain deflagration of a composite oxidizer containing as little as 0.02 weight percent of potassium dichromate. This is nearly an order of magnitude better than previously obtained for any other composition in this apparatus. The work is continuing.

Fundamental studies of the mechanism of synergistic catalysis are being carried out along various lines. The previously published induction period studies on the chloride catalyzed AN decomposition (Inorg. Chem., 4, 173, 1965) have been extended to include the

steady state region of decomposition and measurements of water content. The latter were carried out using an automatic Luft-Fisher direct titration Karl Fisher apparatus. This was found to give a precision of $\pm 1.5\%$ and an accuracy of 0.5% on the systems used.

An M.S. thesis written on this work reports the first detailed investigation of changes in the water content and acidity in the chloride-catalyzed decomposition of ammonium nitrate made during flushing and induction periods. The results are concordant with the decomposition mechanism previously proposed and verify the hypotheses put forth earlier regarding the function of flushing gases and the reactions occurring during the induction period.

During flushing the acidity increases initially, and the concentration of water decreases until both reach steady state values. Following flushing the acidity changes in a sigmoid fashion and becomes constant. The water content also increases, slowly at first but at a much greater rate just prior to the rate maximum. In the steady state region, it also becomes relatively constant. The mole ratio of acid to water goes through a maximum during the induction period and remains constant during the steady state.

These facts are consistent with the theory previously developed in this laboratory that during the initial stages of flushing both water and ammonia are volatilized from the melt thus causing the acidity to increase and the water content to decrease. Both of these phenomena cause the length of the induction period to decrease. At longer flushing times, a steady state condition is reached in which both water content and acidity are relatively constant. As soon as flushing is stopped, an increase of acidity again occurs. This increase in acidity catalyzes a corresponding rapid increase in the reaction rate, which in turn results in an increase in the water content. Due to the stoichiometry, water is produced at a faster rate than acidity and its effect as an inhibitor causes the rate to fall off again. Finally, a condition is reached in which the product gases assume the flushing function, and a steady state is reached with respect to the concentrations of all kinetically important species. This material will be written up for publication.

In other fundamental research on the mechanism of synergistic catalysis of AN decomposition by copper and chloride, determination of N_2/N_2O ratios has shown that the catalyst acts first on the N_2 -producing reaction. Only after this accelerated reaction has raised the acidity sufficiently does the catalyst affect the N_2O reaction. Increase in acidity alone is however not sufficient to account for the increase in the N_2O rate. These data and others involving acidity and induction period have been incorporated into a tentative mechanism involving reduction of copper by electron transfer through a hydrogen bonded chloride bridge. This will be developed further during the writing of the M.S. thesis resulting from this research.

The electrometric techniques described in Special Report No. 4 and in previous annual reports are directed toward developing methods of measuring acidity in situ in a decomposing oxidizer. In one area of work, it has been found that a soft glass membrane is not as reproducible for the determination of selectivity constants as was the Pyrex used in earlier work. The soft glass is very sensitive to small acidity changes in AN and to attack by lithium. No suitable buffers could be found. Attempts to work in KNO_3 solvent at 350° resulted in excessive exchange of Ag^+ with the glass and leakage of the fritted reference electrodes. The latter problem also prevented selectivity constants on Pyrex from being measured for monovalent cations in KNO_3 solvent at 350° .

While the numerical values are not very reproducible, the following order for selectivity constants on soft glass in AN solvent at 190° seems to hold: $\text{Ag} > \text{Na} > \text{Li} > \text{K} \approx \text{NH}_4$. This is different from the order previously found for Pyrex which was: $\text{Na} > \text{Ag} > \text{Li} > \text{K} \approx \text{NH}_4$.

Interesting data have also been obtained with a "Stern" type cell using a Pyrex membrane and a binary mixture of AgNO_3 and KNO_3 or LiNO_3 at 350° . Notz had found that in such a cell for the binary mixture AgNO_3 - NaNO_3 , the membrane potential was zero. This could be explained by either the ion-exchange or liquid-junction models under proper assumptions. This is not the case with the present binary systems involving KNO_3 or LiNO_3 . It appears that the data may afford a means of distinguishing between the two models mentioned but mathematical analysis of the situation is not yet complete. This material will also be the subject of an M.S. thesis.

A Ph.D. dissertation is nearly complete which embodies the detailed studies of synergistic catalysis of AN decomposition and is the basis of the patent application. This dissertation includes a complete survey by thermal analysis of the synergistic behavior with chloride of 23 metals, mostly of the transition series. Correlations with physical and chemical parameters of the metal atoms and group location in the periodic table are presented. Also included are data and conclusions regarding the mechanism of specific chromium catalysis as determined by rate studies.

None

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13 ABSTRACT Progress during the year in the investigation of the synergistically catalyzed decomposition of oxidizers such as ammonium nitrate and ammonium perchlorate is summarized. Research has been done in the areas of thermal analysis, catalytic and mechanistic studies, electrometric measurements and water determinations. The synergistic catalytic combinations consist of a stoichiometric excess of chloride ion with various metals (as salts), mostly of the transition series. A patent covering these compositions will be issued in June, 1967.		

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